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(54) Title: **FINELY CRYSTALLINE AND/OR FAST PHOSPHATE CONVERSION COATING COMPOSITION AND PROCESS**

(57) Abstract

A combination of difunctional organic acid, preferably a hydroxy acid such as citric acid, or salt thereof with acrylic acid/acrylate polymers in zinc phosphate conversion coating forming liquid compositions, preferably also containing hydroxylamine, results in crystal size refinement in the coating formed and/or faster formation of a sufficiently thick conversion coating to protect against subsequent rusting of a ferrous substrate.

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Description
**FINELY CRYSTALLINE AND/OR FAST PHOSPHATE CONVERSION
COATING COMPOSITION AND PROCESS**

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to compositions and processes for depositing zinc phosphate containing conversion coatings on metal surfaces, particularly the surfaces of iron, steel, zinc-iron alloy, galvanized steel and other predominantly zinciferous surfaces, and aluminum and its alloys that contain at least 45 % by weight of aluminum. The invention particularly relates to such compositions and processes that produce, at a high coating speed, a conversion coating with a very fine average crystal size.

Statement of Related Art

The general process of zinc phosphate conversion coating is well known in the art. See, e.g., M. Hamacher, "Ecologically Safe Pretreatments of Metal Surfaces", *Henkel-Referate* 30 (1994), pp. 138 - 143, which, except to the extent that it may be contrary to any explicit statement herein, is hereby incorporated herein by reference. In brief, contact of active metals with aqueous acidic compositions containing zinc and phosphate ions results in the deposition on the active metal surfaces of a conversion coating containing zinc phosphate. If the active metal is ferrous, iron phosphates are usually included in the coating, and in modern practice nickel and/or manganese are often included in the coating composition and thereby in the coating formed. In order to speed the process and improve the uniformity of the coating, it is customary to include in the coating composition a component called an "accelerator" that does not usually become incorporated into the coating formed. Typical widely used accelerators include nitrate, nitrite, and chlorate ions, water soluble nitroaromatic organic compounds such as p-nitrobenzene sulfonic acid, and hydroxylamine (the latter almost always in the form of salts or complexes).

A frequently observed problem with prior art conversion coatings, particularly on cold rolled steel, has been the production of small rusty spots on areas of the treated substrate metal that were blocked from full contact with the conversion coating forming liquid composition by small gas bubbles that were formed and/or trapped on the substrate

surface during the conversion coating treatment process. It is believed that the water vapor inside such bubbles is sufficient to cause rusting before the desired formation of a protective conversion coating can progress sufficiently far to prevent rust, and once a rusty spot has formed, it can not usually be covered satisfactorily later even by full contact with the conversion coating forming liquid composition.

DESCRIPTION OF THE INVENTION

Object of the Invention

One object of this invention is to provide a composition and process for phosphating that will provide a protective conversion coating with a more refined crystal size than is now generally achieved by zinc phosphating. Another alternative or concurrent object is to provide a zinc phosphating composition and process that will form a high quality protective conversion coating during a brief contact time with a metal substrate to be coated, so that coil coating and other continuous phosphating operations can be run at higher speeds. Still another concurrent or alternative object is to avoid the formation of surface rust on small areas of the treated substrate that are blocked by gas bubbles from full contact with the conversion coating solution. Other objects will be apparent from the description below.

General Principles of Description

Except in the claims and the operating examples, or where otherwise expressly indicated, all numerical quantities in this description indicating amounts of material or conditions of reaction and/or use are to be understood as modified by the word "about" in describing the broadest scope of the invention. Practice within the numerical limits stated is generally preferred, however. Also, throughout the description and claims, unless expressly stated to the contrary: percent, "parts of", and ratio values are by weight; the description of a group or class of materials as suitable or preferred for a given purpose in connection with the invention implies that mixtures of any two or more of the members of the group or class are equally suitable or preferred; description of constituents in chemical terms refers to the constituents at the time of addition to any combination specified in the description, and does not necessarily preclude chemical interactions among the constituents of a mixture once mixed; specification of materials in ionic form implies the presence of sufficient counterions to produce electrical neutrality for the composition as a whole; any counterions thus implicitly specified

should preferably be selected from among other constituents explicitly specified in ionic form, to the extent possible; otherwise such counterions may be freely selected, except for avoiding counterions that act adversely to the objects of the invention; the terms "molecule" and "mole" and their grammatical variations may be applied to ionic, elemental, or any other type of chemical entities defined by the number of atoms of each type present therein, as well as to substances with well-defined neutral molecules; the first definition of an acronym or other abbreviation applies to all subsequent uses herein of the same abbreviation; and the term "polymer" includes "oligomer", "homopolymer", "copolymer", "terpolymer", and the like.

10 Summary of the Invention

It has been found that one or more of the objects stated above for the invention can be achieved by the use of a conversion coating forming aqueous liquid composition that comprises, preferably consists essentially of, or more preferably consists of, water and:

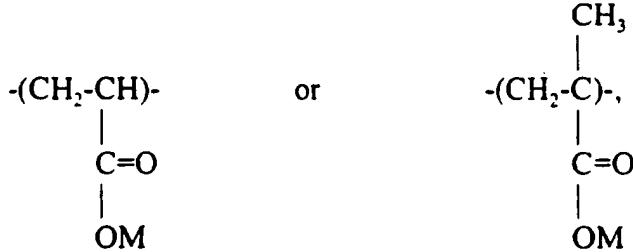
15 (A) dissolved zinc cations;

(B) dissolved phosphate anions;

(C) a dissolved component selected from the group consisting of organic acids and anions thereof that (i) contain at least two moieties per molecule that are selected from the group consisting of carboxyl and carboxylate moieties and hydroxyl moieties that are not part of a carboxyl moiety and (ii) do not contain more than 20 12 carbon atoms per molecule; and

(D) a dissolved component selected from the group consisting of polymer molecules which contain more than 12 atoms per molecule and in which at least 50 % of the polymer molecule is made up of one or more moieties with one of the formulas:

25



30

where M represents a hydrogen atom, a monovalent cation, or a monovalent fraction of a polyvalent cation; and, optionally,

(E) a component of dissolved metal cations selected from the group consisting of

metal cations, exclusive of zinc cations, with a charge of at least two;

- (F) a component of dissolved accelerator molecules, exclusive of any molecules that are part of any of the preceding components; and
- (G) a component of dissolved simple and/or complex fluoride anions, exclusive of any anions that are part of any of the preceding components.

Various embodiments of the invention include working compositions for direct use in treating metals, make-up concentrates from which such working compositions can be prepared by dilution with water, replenisher concentrates suitable for maintaining optimum performance of working compositions according to the invention, processes for treating metals with a composition according to the invention, and extended processes including additional steps that are conventional *per se*, such as cleaning, activation with titanium phosphate sols (Jernstedt salts), rinsing, and subsequent painting or some similar overcoating process that puts into place an organic binder containing protective coating over the metal surface treated according to a narrower embodiment of the invention. Articles of manufacture including surfaces treated according to a process of the invention are also within the scope of the invention.

Description of Preferred Embodiments

For a variety of reasons, it is sometimes preferred that compositions according to the invention as defined above should be substantially free from many ingredients used in compositions for similar purposes in the prior art. Specifically, when maximum storage stability of a concentrate is desired, it is preferred, with increasing preference in the order given, independently for each preferably minimized component listed below, that these compositions contain no more than 25, 15, 9, 5, 3, 1.0, 0.35, 0.10, 0.08, 0.04, 0.02, 0.01, 0.001, or 0.0002, percent of each of the following constituents: nitrite, chlorate, chloride, bromide, iodide, organic compounds containing nitro groups, hexavalent chromium, manganese in a valence state of four or greater, ferricyanide; ferrocyanide; and pyrazole compounds. In contrast, in working solutions, accelerator components such as those included in this list have no known detrimental effect (except for the danger of white specking zinciferous surfaces treated with compositions that contain too much chloride, which is formed *in situ* from chlorate), but are generally not needed, and their absence may therefore be preferred for economic reasons.

The dissolved zinc cations required for necessary component (A) may be obtained

from any soluble zinc salt or from zinc metal itself or any zinc containing compound that reacts with aqueous acid to form dissolved zinc cations. Normally preferred sources, largely for economic reasons, are zinc oxide, zinc carbonate, and zinc dihydrogen phosphate. In a working conversion coating forming aqueous liquid composition according to the invention, the concentration of dissolved zinc cations preferably is at least, with increasing preference in the order given, 0.1, 0.2, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.85, 0.90, 0.95, 0.98, or 1.00 parts per thousand (hereinafter usually abbreviated as "ppt") and independently preferably is not more than, with increasing preference in the order given, 2.0, 1.8, 1.6, 1.4, 1.30, 1.20, 1.15, or 1.10 ppt.

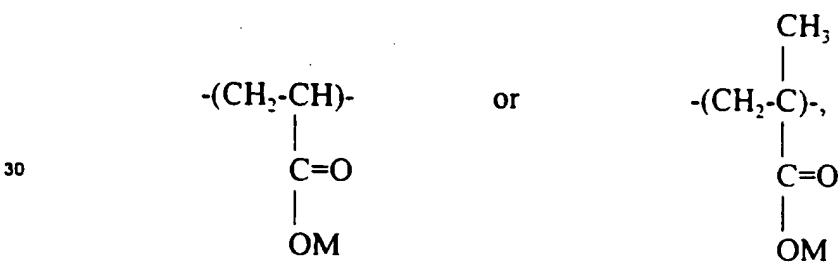
The dissolved phosphate ions that constitute necessary component (B) also may be obtained from a variety of sources as known in the general phosphate conversion coating art. Because of a preference noted below for a substantial amount of total acid in a working conversion coating forming aqueous liquid composition according to the invention, normally much of the phosphate ion content will preferably be supplied by phosphoric acid added to the composition, and the stoichiometric equivalent as phosphate ions of all undissociated phosphoric acid and all its anionic ionization products in solution, along with the stoichiometric equivalent as phosphate ions of any dihydrogen phosphate, monohydrogen phosphate, or completely neutralized phosphate ions added to the composition in salt form, are to be understood as forming part of component (B), irrespective of the actual degree of ionization that exists in the composition. In a working conversion coating forming aqueous liquid composition according to the invention, the concentration of component (B) preferably is at least, with increasing preference in the order given, 5, 6, 7, 8, 9, 10, 10.5, 11.0, 11.5, 11.9, 12.2, 12.4, 12.6, 12.8, 13.0, 13.2, 13.4, or 13.6 ppt and independently preferably is not more than, with increasing preference in the order given, 100, 50, 40, 30, 27, 24, 21, 19, 18, 17, 16.5, 16.0, 15.5, 15.0, 14.5, 14.3, 14.1, 13.9, or 13.7 ppt.

Independently of the other preferences, the ratio of the concentration of component (A) to the concentration of component (B) in a conversion coating forming aqueous liquid composition according to the invention, whether working or concentrate, preferably is at least, with increasing preference in the order given, 1.0:50, 1.0:40, 1.0:35, 1.0:30, 1.0:27, 1.0:24, 1.0:21, 1.0:18, 1.0:16, 1.0:15, 1.0:14, or 1.0:13.7 and independently preferably is not more than, with increasing preference in the order given, 1.0:5.0, 1.0:6.0.

1.0:7.0, 1.0:8.0, 1.0:8.5, 1.0:9.0, 1.0:9.5, 1.0:10, 1.0:10.5, 1.0:11.0, 1.0:11.5, 1.0:12.0, 1.0:12.5, 1.0:13.0, or 1.0:13.3.

Component (C) is preferably derived from anions or other molecules each of which contains both at least one carboxyl(ate) moiety and one hydroxyl moiety that is not part of any carboxyl(ate) moiety, more preferably from the group consisting of citric acid, gluconic acid, and heptogluconic acid and the water soluble salts of all of these acids, most preferably from citric acid and its water soluble salts. Independently, the concentration of component (C) in a working conversion coating forming aqueous liquid composition according to the invention preferably is at least, with increasing preference in the order given, 0.1, 0.2, 0.3, or 0.4 millimoles per kilogram of total composition (hereinafter usually abbreviated "mM/kg") and, if small crystal size of the conversion coating formed is desired, more preferably is at least, with increasing preference in the order given, 1.0, 1.2, or 1.6 mM/kg; if small crystal size of the conversion coating formed is desired and the concentration of component (D) is near the lower end of its preferred ranges as further described below, the concentration of component (C) in a working conversion coating forming aqueous liquid composition according to the invention still more preferably is at least 3.5 mM/kg. Independently, primarily for reasons of economy, the concentration of component (C) in a working composition according to the invention preferably is not more than, with increasing preference in the order given, 50, 25, 15, 10, 7, 5, 4.5, or 4.1 mM/kg, and if larger crystal size is acceptable, more preferably is not greater than, with increasing preference in the order given, 3.2, 3.0, 2.8, 2.5, 2.2, 1.9, or 1.7 mM/kg.

Component (D) preferably is selected from polymer molecules in which at least, with increasing preference in the order given, 60, 70, 75, 80, 85, 90, or 95 % of the molecule consists of one or more moieties with one of the formulas:



more preferably the formula shown on the left, or in other words, acrylate rather than methacrylate moieties. Independently, with increasing preference in the order given, at

least 30, 50, 60, 70, or 80 number percent of these acrylate and methacrylate moieties in component (D) have hydrogen rather than any other atom or cation in the position in the formula indicated by the symbol "M" in the formulas shown. Independently of both other preferences, the weight average molecular weight of the polymers in the component (D), measured as its stoichiometric equivalent when all the acrylate and methacrylate moieties are in an acid form, preferably is at least, with increasing preference in the order given, at least 400, 500, 600, 700, 750, 800, 850, 900, 950, or 975 and independently preferably is not more than, with increasing preference in the order given, 10,000, 9000, 8000, 7000, 6000, 5000, 4500, 4000, 3500, 3000, 2500, 2000, 1700, 1400, 1300, 1250, 1200, 1150, 1100, or 1050. Also, independently of the other preferences for component (D), the concentration of component (D) in a working conversion coating forming aqueous liquid composition according to the invention preferably is at least 5, 10, 15, 20, 22, or 24 ppm and independently preferably is not more than 300, 200, 100, 85, 75, 65, or 55 ppm and, unless the concentration of component (C) is not more than 0.4 mM/kg, more preferably is not more than, with increasing preference in the order given, 45, 35, 30, or 26 ppm.

If high corrosion resistance after application of an organic protective coating to a metal substrate, subsequent to forming a conversion coating thereon by contacting the substrate with a working conversion coating forming aqueous liquid composition according to the invention, is desired, as it usually is, a working conversion coating forming aqueous liquid composition according to the invention preferably contains one or more metal ions selected from optional component (E). Examples of preferred combinations of zinc ions with metal ions of component (E) in a working conversion coating forming aqueous liquid composition according to the invention are: Zn and Mn; Zn, Mn, and Co; Zn, Mn, and Cu; Zn and Cu; Zn, Co, and Cu; and Zn, Mn, and Ni. It is especially preferred for a working conversion coating forming aqueous liquid composition according to the invention to contain, as at least part of optional component (E), dissolved divalent manganese cations in a concentration that preferably is at least, with increasing preference in the order given, 100, 200, 300, 400, 500, 550, 600, 650, 700, 750, 800, 825, or 835 ppm and independently preferably is, primarily for reasons of economy, not more than, with increasing preference in the order given, 4000, 3000, 2000, 1500, 1400, 1300, 1250, 1200, 1150, 1100, 1050, 1000, 950, or 900 ppm. Also, independently of the prefer-

ences for manganese as noted, it is especially preferred for a working conversion coating forming aqueous liquid composition according to the invention to include, as at least part of optional component (E), dissolved divalent nickel cations in a concentration that preferably is at least, with increasing preference in the order given, 100, 200, 300, 400, 500, 550, 600, 650, 700, 750, 765, 785, or 790 ppm and independently preferably is, primarily for reasons of economy, not more than, with increasing preference in the order given, 4000, 3000, 2000, 1500, 1400, 1300, 1250, 1200, 1150, 1100, 1050, 1000, 950, 900, or 850 ppm.

Independently of other preferences, the ratio of the concentration of zinc cations to the sum of the concentrations of manganese and nickel cations in a conversion coating forming aqueous liquid composition according to the invention preferably is at least, with increasing preference in the order given, 1.0:5.0, 1.0:4.0, 1.0:3.5, 1.0:3.0, 1.0:2.5, 1.0:2.3, 1.0:2.1, 1.0:1.9, 1.0:1.7, or 1.0:1.6 and independently preferably is not more than, with increasing preference in the order given, 1.0:0.2, 1.0:0.4, 1.0:0.6, 1.0:0.8, 1.0:1.0, 1.0:1.1, 1.0:1.2, 1.0:1.3, 1.0:1.4, or 1.0:1.5. Independently, when both manganese and nickel are present in a conversion coating forming aqueous liquid composition according to the invention, the ratio of manganese to nickel preferably is at least, with increasing preference in the order given, 1.0:2.0, 1.0:1.7, 1.0:1.5, 1.0:1.3, 1.0:1.2, 1.0:1.1, or 1.0:1.0 and independently preferably is not more than, with increasing preference in the order given, 1.0:0.2, 1.0:0.5, 1.0:0.7, 1.0:0.8, or 1.0:0.9.

A working conversion coating forming aqueous liquid composition according to the invention preferably includes, as at least part, and more preferably as all, of optional component (F) a dissolved source of hydroxylamine. The source may be hydroxylamine itself, but most users prefer to avoid potential hazards from handling pure hydroxylamine, so that a salt or complex of hydroxylamine is generally preferred. Hydroxylamine sulfate, which has the chemical formula $(\text{NH}_3\text{OH})_2\text{SO}_4$, is particularly preferred for economy and lack of any ions that may be deleterious to the quality of conversion coating formed, e.g., chloride ions, which may induce white specking of any zinc-rich areas of the coated substrate. Irrespective of its actual source, the concentration in a working conversion coating forming aqueous liquid composition according to the invention, measured as its stoichiometric equivalent as pure hydroxylamine, preferably is at least, with increasing preference in the order given, 0.2, 0.5, 0.8, 1.0, 1.1, 1.2, 1.3, 1.4, or 1.5 ppt and independ-

ently preferably is not more than, with increasing preference in the order given, 5, 4, 3.5, 3.0, 2.5, 2.3, 2.1, 1.9, or 1.8 ppt.

If the surface of the substrate to be conversion coated according to this invention includes a portion that contains at least 45 % of aluminum and/or a portion that contains at least 85 % of zinc, a working conversion coating forming aqueous liquid composition according to the invention preferably includes optional simple and/or complex fluoride anions component (G); more preferably, if the substrate surface includes a portion that contains at least 85 % of zinc, at least part of the fluoride present is in the form of fluoboric, fluosilicic, fluotitanic, and/or fluozirconic acids and their salts, most preferably fluosilicic acid and/or fluosilicate ions.

Because of the competing complex-forming-and-dissociating equilibria in which fluoride can participate in a working conversion coating forming aqueous liquid composition according to this invention that contains some deliberately added complex fluometallate and/or hydrofluoric acid, the preferable concentrations for fluoride in such a composition are specified in terms of "active free fluoride", as measured by means of a fluoride sensitive electrode and associated instrumentation and methods that are described in U. S. Patents 3,350,284 and 3,619,300. Suitable apparatus and instructions for using it are commercially available under the name LINEGUARD® 101A Meter from the Parker Amchem Division ("PAM") of Henkel Corp., Madison Heights, MI. "Active free fluoride" as this term is used herein was measured relative to a 120E Activity Standard Solution also commercially available from PAM. In brief, the fluoride sensitive electrode and the reference electrode provided with the LINEGUARD® 101A Meter are both immersed in the noted Standard Solution and the millivolt meter reading is adjusted to 0 with a Standard Knob on the instrument, after waiting if necessary for any drift in readings to abate. The electrodes are then rinsed with deionized or distilled water, dried, and immersed in the sample to be measured, which should be brought to the same temperature as the noted Standard Solution had when it was used to set the meter reading to 0. The reading of the electrodes immersed in the sample is taken directly from the millivolt (hereinafter often abbreviated "mv" or "mV") meter on the instrument and converted to ppm by comparison with the millivolt readings obtained with solutions of known free fluoride content, usually sodium or potassium fluoride solutions in water.

The free fluoride content of a working conversion coating forming aqueous liquid

composition according to the invention, when a surface including areas that are at least 45 % aluminum is being treated, preferably is at least, with increasing preference in the order given, 100, 150, 200, 250, 300, 350, 375, or 400 ppm and independently preferably is not more than, with increasing preference in the order given, 1200, 1000, 900, 800, 750, 725, 700, 675, 650, 625, or 600 ppm. If a surface including areas that are at least 85 % zinc but no areas that are at least 45 % aluminum is to be treated, the free fluoride content preferably is not more than, with increasing preference in the order given, 100, 75, 60, 45, 40, 35, 30, 25, 20, 15, or 10 ppm, but the total content of fluoborate, fluosilicate, fluotitanate, and fluozirconate, which includes the stoichiometric equivalent as these ions of all corresponding acids and partially acidic salts added to the compositions, irrespective of the actual degree of ionization existing in the composition, preferably is at least, with increasing preference in the order given, 0.1, 0.3, 0.5, 0.7, 0.8, 0.9, 1.00, 1.10, 1.15, or 1.20 ppt and independently preferably is, primarily for reasons of economy and with increasing preference in the order given, not more than 3.0, 2.5, 2.0, 1.8, 1.6, 1.50, 1.45, 1.40, 1.35, or 1.30 ppt. Most preferably, the total amount of these complex fluoride anions is fluosilicate or its corresponding acid or acid salt. When the surfaces being treated are ferrous and do not include any areas that are predominantly either aluminum or zinc, fluoride may be omitted altogether, and such omission is normally preferred for economic reasons. If any fluoride is present in the working compositions according to the invention for treating only ferrous substrates, the same preferences as noted above for the maximum amount of free fluoride activity in a composition for treating aluminum-free zinciferous surfaces apply.

In a working conversion coating forming aqueous liquid composition according to the invention, the Total Acid and Free Acid contents of the composition are preferably measured and controlled. These acid contents, consistent with general practice in the phosphating art, are expressed herein in "points", by which is meant the milliliters ("ml") of 0.1 N NaOH required to titrate a 10 ml aliquot sample, to a pH of 8.2 (e.g., with phenolphthalein indicator) for Total Acid and to a pH of 3.8 (e.g., with bromophenol blue indicator) for Free Acid.

In a working conversion coating forming aqueous liquid composition according to the invention, the content of Free Acid preferably is at least, with increasing preference in the order given, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, or 1.0 points and inde-

pendently preferably is not more than, with increasing preference in the order given, 3.0, 2.5, 2.0, 1.8, 1.7, 1.6, or 1.5 points; and, independently, the content of Total Acid preferably is at least, with increasing preference in the order given, 15, 16, 17, 18, 19, 20, or 21 points and independently preferably is not more than, with increasing preference in the order given, 50, 40, 35, 32, 30, 29, or 28 points. The Free Acid and Total Acid contents can be adjusted into the preferred range, without disturbing the preferred values for other constituents of a conversion coating forming aqueous liquid composition according to the invention, by additions, to an otherwise satisfactory conversion coating forming aqueous liquid composition, of small amounts of strongly alkaline materials such as sodium and potassium hydroxides or strong acids such as nitric and sulfuric acids, as appropriate for the direction in which it is desired to change the Free Acid and Total Acid contents, in a manner generally known to those skilled in the art.

Preferably make-up concentrate compositions according to this invention are single package liquid concentrates, i.e., are aqueous liquids that consist of water and each of components (A) through (G), as recited above for working compositions, that are desired in the working compositions to be prepared from the make-up concentrate compositions, along with any other ingredients desired in the working compositions, except possibly for strong acids or alkalies that are not part of any of components (A) through (G) and are added to working compositions after preparation thereof to slightly less than the final desired volume, in order to adjust the Free Acid and Total Acid contents therein as defined above. Preferably, all the components except water of a make-up concentrate composition according to the invention are present therein in a concentration such that the ratio of the concentration of each component in the make-up concentrate composition to the concentration of the same component in the working composition that it is desired to prepare from the concentrate composition will be at least, with increasing preference in the order given, 5:1.0, 10:1.0, 20:1.0, 30:1.0, 40:1.0, or 50:1.0.

Preferably the concentrates are stable to storage in the temperature range from at least -20 to 50, or more preferably to 80, °C. Stability may conveniently be evaluated by measuring the free acid and total acid contents as described above. If these values have not changed after storage by more than 10 % of their value before storage, the concentrate is considered storage stable. With increasing preference in the order given, the concentrates according to the invention will be storage stable as thus defined after stor-

age for 1, 3, 10, 30, 60, or 200 days.

The actual conversion coating forming step in a process according to this invention preferably is performed at a temperature that is at least, with increasing preference in the order given, 35, 38, 41, 44, 46, or 48 °C and independently preferably is, primarily for reasons of economy, not more than 70, 65, 60, 55, 53, 51, or 50 °C. Primarily for reasons of economy, the time of contact between the metal surface being coated and a working composition according to the invention preferably is not greater than, with increasing preference in the order given, 200, 150, 120, 100, 80, 70, 60, 50, 40, 30, 25, 20, 17, 14, 11, 9.0, 7.0, 5.0, 4.0, 3.0, or 2.0 seconds, if a uniform and adequately protective coating is formed within that time. Otherwise, a process according to this invention is preferably operated under the conditions conventional in the art for compositions that are otherwise like the compositions according to this invention, except for substituting a conventional amount of nitrite accelerator for all of the hydroxylamine, acrylate and/or methacrylate polymer, and at least difunctional acids and/or hydroxyacids described above for compositions according to this invention. Furthermore, in a process according to the invention that includes other steps than zinc phosphate conversion coating with a composition as described above, the other steps preferably are conventional *per se*.

The practice of this invention may be further appreciated by consideration of the following, non-limiting, working examples and comparison examples.

General Processing Conditions

The substrates used and their abbreviations as used in later tables are shown in Table 1 below. The substrates were in the form of conventional rectangular test panels.

The processing sequence used is shown in Table 2 and its notes. All materials identified by one of the trademarks DEOXYLYTE®, FIXODINE®, or PARCO® are commercially available from the Parker Amchem Division of Henkel Corp., Madison

Table 1

Substrate Metal Type	Abbreviation
Cold rolled steel	CRS
One side electrogalvanized steel	1EG
Hot dip galvanized steel	HDG
Both sides electrogalvanized steel	2EG
Zinc-iron alloy	Z-I

Table 2

Process Action	Fluid Used	Temp., °C	Time, Sec.
Spray Primary Cleaning	21 g/L of PARCO® Cleaner 1502 in water	49	90
Spray Rinse	Tap Water	49	30
Activation	FIXODINE® Z-8 Conditioner, 11 ppm Ti	20 - 25	30
Phosphating	See later tables	49	10, 120*
Spray Rinse	Tap Water	20 - 25	30
Postrinsing	0.25 % DEOXYLYTE® 54 NC Postrinse in water	20 - 25	30
Spray Rinse	Deionized water	20 - 25	15

Footnote for Table 2

*The entire panel was dipped into the phosphating composition for 10 seconds. Then the top half of the panel was withdrawn. The bottom half remained immersed for a total of 120 seconds, and the entire panel was then withdrawn from contact with the phosphating composition.

Abbreviations for Table 2

Temp. = Temperature; Sec. = Seconds.

Heights, Michigan and/or Henkel Metallchimie, Düsseldorf, Germany, together with directions for using them as noted below.

Working Phosphating Compositions

The most important components of several working compositions are shown in Table 3; the balance not shown in the table is water or counterions, the latter being predominantly sodium to serve as counterions to a substantial fraction of the phosphate content. Aqueous sodium hydroxide solution was used when needed to lower free acid content. Nitric acid was added in small quantities as the concentration of citrate was increased, to avoid unwanted decreases in free acid content without changing the zinc to phosphate ratio. Any free fluoride content indicated in the Table by a specific number was measured by a fluoride sensitive electrode in the manner described above and was added as hydrofluoric acid. Free fluoride contents preceded by the "less than" sign (<) were measured in the same way, but also mean that no hydrofluoric acid or other known source of uncomplexed fluoride was deliberately added; the free fluoride activity presumably arose from small concentrations of hydrofluoric acid known to exist in the fluosilicic acid that was deliberately added. The source of the acrylate polymer shown in Table 3 was Acusol™ 410 polymer solution in water, a product commercially supplied by Rohm & Haas Co. and reported by its supplier to contain 54 % by weight of a homopolymer of acrylic acid in which 20 number % of the carboxylic moieties are neutralized with sodium hydroxide, the polymer in the all acid form having a weight average molecular weight of 1000 and a number average molecular weight of 650.

Table 3

Ingredient and Concentration Unit	Amount of Ingredient in Composition Example Number:									
	1	2	3	4	5	6	7	8	9	10
Zn ⁺² ions, ppt	1.1	1.1	1.1	1.1	1.05	1.1	1.1	1.01	1	1
PO ₄ ⁻³ ions, ppt	14	14	14	14	13.7	14	14	13.7	14	14
Mn ⁺² ions, ppt	0.8	0.8	0.8	0.8	0.81	0.8	0.8	0.84	0.8	0.8
Ni ⁺² ions, ppt	0.8	0.8	0.8	0.8	0.78	0.8	0.8	0.8	0.8	0.8
Sodium citrate dihydrate, ppt	Slt.	Slt.	Slt.	Slt.	Slt.	Slt.	Slt.	Slt.	Slt.	Slt.
(NH ₃ OH) ₂ SO ₄ , ppt	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Free Acid, points	1.5	1.7	1.0	1.0	1.0	1.0	1.5	1.0	0.7	0.6
Total Acid, points	27	28	27	21	25	27	27	26	27	27
Acrylate polymer, ppm	10	10	10	25	25	25	25	50	50	50
H ₂ SiF ₆ , ppt	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
Free F activity, ppm	690	690	690	<25	<25	680	680	670	670	670

Abbreviation for Table 3

Slt. = See later table(s).

The citrate concentrations in the working phosphating compositions and the resulting coating weights and crystal sizes are shown in Tables 4 - 11.

Table 4: RESULTS WITH 10 PPM OF ACRYLATE POLYMER ON CRS SUBSTRATES

Comp. #	Citrate Conc.	Coating Weights, g/m ²		Crystal Size, μ	Other Observa- tions
		Top	Bottom		
1	0.10	1.10	2.62	8 - 10	SRD
1	0.20	1.17	2.83	5 - 8	SRD
2	0.30	0.70	2.90	5 - 8	SRD
3	0.30	1.57	2.67	5 - 8	SRD
3	0.40	0.96	2.68	5 - 8	SRD
3	0.50	0.99	2.86	3 - 5	SRD
3	0.65	1.30	2.87	3 - 5	SRD
3	0.80	1.38	2.71	3 - 5	DVSR
3	1.00	1.04	2.52	3	D

Additional Abbreviations for Table 4

(See notes for previous tables and main text for others)

Comp. # = Composition Number (from Table 3); Conc. = Concentration; g/m² = grams per square meter; μ = micrometres; SRD = Surface rust and dusting observable after phosphating; DVSR = Dusting and very slight surface rust observable after phosphating; D = Dusting but no rust observable after phosphating.

Table 5: RESULTS WITH 10 PPM OF ACRYLATE POLYMER ON 1EG SUBSTRATES

Comp. #	Citrate Conc.	Coating Weight, g/m ²				Crystal Size, μ		Other Observations	
		OSS		OGS		OSS	OGS		
		Top	Bottom	Top	Bottom				
1	0.10	1.12	3.01	2.88	2.82	5 - 10	~ 10	D	
1	0.20	0.88	2.80	2.83	2.97	5 - 10	~ 8	D	
2	0.30	0.70	3.07	2.97	2.76	5 - 10	5 - 10	D	
3	0.30	1.59	2.43	2.14	2.78	5 - 10	5 - 10	D	
3	0.40	1.14	2.66	2.80	2.83	5 - 10	N.m.	D	
3	0.50	1.22	2.40	3.06	2.68	8	5 - 10	D	
3	0.65	1.27	2.37	2.65	2.72	6	5	D	
3	0.80	1.14	2.10	2.72	2.71	5	5	D	
3	1.00	1.00	2.07	2.11	2.44	5	3	D	

Additional Abbreviations for Table 5 (See notes for previous tables and main text for others)

OSS = On steel side; OGS = On galvanized side; N.m. = Not measured.

Table 6: RESULTS WITH 10 PPM OF ACRYLATE POLYMER ON OTHER SUBSTRATES

On HDG Substrate			On 2EG Substrate			On Z-I Substrate		
Coat. Wt., g/m ²		Crystal Size, μ	Coat. Wt., g/m ²		Crystal Size, μ	Coat. Wt., g/m ²		Crystal Size, μ
Top	Bottom		Top	Bottom		Top	Bottom	
2.96	2.84	10	3.08	2.52	5	2.13	4.10	15 - 20

Additional Abbreviation for Table 6 (See notes for previous tables and main text for others)

Coat. Wt. = Coating Weight

General Note for Table 6

The phosphating composition used for all results in this table was Number 3 from Table 3 with 1.00 ppt of citrate. No surface rust or dusting of the coating was observed.

Table 7: RESULTS WITH 25 PPM OF ACRYLATE POLYMER ON CRS SUBSTRATES

Comp. #	Citrate Conc.	Coating Weights, g/m ²		Crystal Size, μ	Other Observa- tions
		Top	Bottom		
4	0.00*	0.61*	2.08*	15 - 20*	SRD*
4	0.10	0.93	3.76	15 - 20	SRD
4	0.20	1.22	3.62	10 - 15	SRD
4	0.30	1.04	3.15	8 - 10	SRD
5	0.30	1.30	2.85	5 - 10	SRD
5	0.40	1.35	2.82	5 - 10	SRD
5	0.50	1.24	2.99	5 - 10	DVSR
6	0.50	1.09	3.35	3 - 6	D
7	0.50	0.34	2.1±0.7	3 - 6	DVSR

Footnote for Table 7

*Comparison example, not according to the invention.

Table 8: RESULTS WITH 25 PPM OF ACRYLATE POLYMER ON 1EG SUBSTRATES

Comp. #	Citrate Conc.	Coating Weight, g/m ²				Crystal Size, μ , OGS	Other Observations		
		OSS		OGS					
		Top	Bottom	Top	Bottom				
4	0.00*	0.66*	2.24*	2.51*	3.28*	10 - 15*	SRD*		
4	0.10	1.09	4.47	2.73	3.14	8 - 10	D		
4	0.20	1.04	4.73	3.29	3.10	8 - 10	D		
4	0.30	0.91	4.06	3.29	3.15	5 - 8	D		
5	0.30	1.36	3.18	2.76	2.90	5 - 8	D		
5	0.40	1.34	3.19	2.85	2.96	5 - 8	D		
5	0.50	1.52	3.18	2.78	3.04	5 - 8	D		
6	0.50	0.83	5.08	2.38	3.95	5	D		
7	0.50	0.69	2.98	3.71	3.77	5	D		

Footnote for Table 8

*Comparison example, not according to the invention.

Table 9: RESULTS WITH 25 PPM OF ACRYLATE POLYMER ON OTHER SUBSTRATES

Comp. #	Citrate Conc.	On HDG Substrate		On 2EG Substrate		On Z-I Substrate	
		Coat. Wt., g/m ²		Coat. Wt., g/m ²		Coat. Wt., g/m ²	
		Top	Bottom	Top	Bottom	Top	Bottom
4	0.30	1.68	3.04	3.13	2.93	0.41	3.49
7	0.50	3.38	2.81	3.25	3.27	0.64	4.66

General Note for Table 9

Surface dusting but no rust after phosphating was observed for both examples in this table.

Table 10: RESULTS WITH 50 PPM OF ACRYLATE POLYMER ON CRS SUBSTRATES

Comp. #	Citrate Conc.	Coating Weights, g/m ²		Crystal Size, μ	Other Observa- tions
		Top	Bottom		
8	0.10	1.06	1.87	8 - 10	DVS
9	0.10	0.58	2.81	8 - 10	SRD
10	0.15	1.05	4.80	8 - 10	SRD
9	0.20	0.93	3.64	8 - 10	SRD

Table 11: RESULTS WITH 50 PPM OF ACRYLATE POLYMER ON IEG SUBSTRATES

Comp. #	Citrate Conc.	Coating Weight, g/m ²				Crystal Size, μ		Other Observa- tions	
		OSS		OGS		OSS	OGS		
		Top	Bottom	Top	Bottom				
8	0.10	0.48	2.62	3.11	4.21	10	15	D	
9	0.10	1.04	4.71	4.02	4.20	8 - 10	15	D	
10	0.15	0.91	3.02	3.84	4.27	8 - 10	10	D	
9	0.20	0.69	3.75	3.79	3.84	8	5	D	

CLAIMS

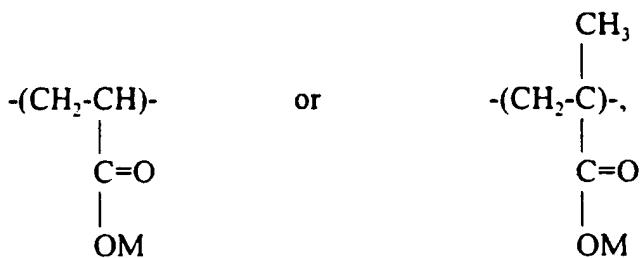
1. An aqueous liquid composition of matter suitable either as such or after dilution with water for forming a phosphate conversion coating on a metal substrate by contact therewith, said composition comprising water and:

5 (A) a concentration of dissolved zinc cations;

(B) a concentration of dissolved phosphate anions;

(C) a concentration of a dissolved component selected from the group consisting of 10 organic acids and anions thereof that (i) contain at least two moieties per molecule that are selected from the group consisting of carboxyl and carboxylate moieties and hydroxyl moieties that are not part of a carboxyl group and (ii) do not contain more than 12 carbon atoms per molecule; and

15 (D) a concentration of a dissolved component selected from the group consisting of polymer molecules which contain more than 12 atoms per molecule and in which at least 50 % of the polymer molecules is made up of one or more moieties with one of the general chemical formulas:



where M represents a hydrogen atom, a monovalent cation, or a monovalent fraction of a polyvalent cation.

25 2. An aqueous liquid composition of matter according to claim 1, wherein: the concentration of component (A) has a ratio to the concentration of component (B) that is from about 1.0:40 to about 1.0:5.0; component (C) is selected from the group consisting of anions and molecules each of which contains both at least one carboxyl or carboxylate moiety and at least one hydroxyl moiety that is not part of any carboxyl or carboxylate moiety; at least about 30 number % of the moieties "M" shown in the general chemical formulas in claim 1 for component (D) are hydrogen; component (D) has a weight average molecular weight from about 500 to about 9000; and the composition additionally comprises at least one of divalent manganese and divalent

nickel cations in a total amount such that the concentration of zinc cations has a ratio to the total amount of divalent manganese and divalent nickel cations that is from about 1.0:3.5 to about 1.0:0.6.

3. An aqueous liquid composition of matter according to claim 2, wherein: the ratio of the concentration of component (A) to the concentration of component (B) is from about 1.0:18 to about 1.0:10; at least about 60 number % of said moieties "M" are hydrogen; at least about 60 % of component (D) consists of acrylate moieties; component (D) has a weight average molecular weight from about 700 to about 1300; the composition comprises both dissolved divalent manganese and divalent nickel cations in concentrations such that the concentration of manganese has a ratio to the concentration of nickel that is from about 1.0:1.5 to about 1.0:0.7; and the ratio of the concentration of zinc cations to the total amount of divalent manganese and divalent nickel cations is from about 1.0:3.5 to about 1.0:0.6.

4. An aqueous liquid composition according to claim 2, wherein: the concentration of component (A) is from about 0.30 to about 2.0 ppt; the concentration of component (B) is from about 6 to about 50 ppt; the concentration of component (C) is from about 0.2 to about 25 mM/kg; the concentration of component (D) is from about 5 to about 200 ppm; and the concentration of dissolved divalent manganese cations is from about 300 to about 3000 ppm.

5. An aqueous liquid composition according to claim 4, wherein: the concentration of component (A) is from about 0.50 to about 1.8 ppt; the concentration of component (B) is from about 8 to about 30 ppt; the concentration of component (C) is from about 0.3 to about 15 mM/kg; the concentration of component (D) is from about 10 to about 100 ppm; the concentration of dissolved divalent manganese cations is from about 500 to about 2000 ppm.

6. An aqueous liquid composition according to claim 5, wherein: the concentration of component (A) is from about 0.60 to about 1.6 ppt; the concentration of component (B) is from about 10 to about 21 ppt; the ratio of the concentration of component (A) to the concentration of component (B) is from about 1.0:30 to about 1.0:8.0; the concentration of component (C) is from about 0.4 to about 10 mM/kg; at least about 70 % of component (D) consists of acrylate and methacrylate moieties, of which at least

50 number % have hydrogen as said moieties "M"; the weight average molecular weight of component (D) is from about 700 to about 7000; the concentration of component (D) is from about 15 to about 85 ppt; the concentration of dissolved divalent manganese cations is from about 600 to about 1500 ppm; and the stoichiometric equivalent concentration of hydroxylamine is from about 1.0 to about 5 ppt.

7. An aqueous liquid composition according to claim 6, wherein: the concentration of component (A) is from about 0.70 to about 1.4 ppt; the concentration of component (B) is from about 11.5 to about 19 ppt; the ratio of the concentration of component (A) to the concentration of component (B) is from about 1.0:27 to about 1.0:10.0; component (C) is selected from the group consisting of citric acid, gluconic acid, and heptogluconic acid and the water soluble salts of all of these acids; the concentration of component (C) is from about 1.0 to about 7 mM/kg; at least about 75 % of component (D) consists of acrylate and methacrylate moieties, of which at least about 60 number % have hydrogen as said moieties "M"; the weight average molecular weight of component (D) is from about 750 to about 4500; the concentration of component (D) is from about 15 to about 45 ppm; the concentration of dissolved divalent manganese cations is from about 700 to about 1300 ppm; and the composition additionally comprises a dissolved source of hydroxylamine in an amount to provide a stoichiometric equivalent concentration of hydroxylamine that is from about 1.2 to about 2.3 ppt.

8. An aqueous liquid composition according to claim 7, wherein: the concentration of component (A) is from about 0.80 to about 1.3 ppt; the concentration of component (B) is from about 12.2 to about 17 ppt; the ratio of the concentration of component (A) to the concentration of component (B) is from about 1.0:21 to about 1.0:10.0; the concentration of component (C) is from about 1.2 to about 5 mM/kg; the weight average molecular weight of component (D) is from about 750 to about 3000; the concentration of component (D) is from about 15 to about 35 ppm; the concentration of dissolved divalent manganese cations is from about 750 to about 1200 ppm; and the stoichiometric equivalent concentration of hydroxylamine is from about 1.3 to about 2.1 ppt.

9. An aqueous liquid composition according to claim 8, wherein: the concentration of component (A) is from about 0.85 to about 1.20 ppt; at least about 70 % of component (D) consists of acrylate moieties, of which at least 70 number % have

hydrogen as said moieties "M"; the weight average molecular weight of component (D) is from about 900 to about 1700; the concentration of dissolved divalent manganese cations is from about 800 to about 1000 ppm; and the composition also comprises dissolved nickel cations in a concentration from about 200 to about 1200 ppm.

5. 10. An aqueous liquid composition according to claim 9, wherein: the concentration of component (A) is from about 0.95 to about 1.15 ppt; the concentration of component (B) is from about 13.0 to about 16.0 ppt; the ratio of the concentration of component (A) to the concentration of component (B) is from about 1.0:18 to about 1.0:13.0; component (C) is selected from the group consisting of citric acid, gluconic acid, and heptogluconic acid and the water soluble salts of all of these acids; the concentration of component (C) is from about 1.6 to about 4.1 mM/kg; at least about 80 % of component (D) consists of acrylate moieties, of which at least 80 number % have hydrogen as said moieties "M"; the weight average molecular weight of component (D) is from about 900 to about 1200; the concentration of component (D) is from about 20 to about 30 ppm; the concentration of dissolved divalent manganese cations is from about 800 to about 1000 ppm; the concentration of dissolved nickel cations is from about 600 to about 900 ppm; and the stoichiometric equivalent concentration of hydroxylamine is from about 1.5 to about 1.8 ppt.

11. A process for forming a phosphate conversion coating on a surface selected from the group consisting of at least one of iron, steel, zinc-iron alloy, galvanized steel and other predominantly zinciferous surfaces, and aluminum and its alloys that contain at least 45 % by weight of aluminum, said process comprising contacting the surface with a composition according to claim 10 at a temperature from about 35 to about 70 °C for a time not greater than 100 seconds, said composition according to claim 10 having a 20 Free Acid content from about 1.0 to about 1.5 points, and a Total Acid content from about 20 to about 28 points; wherein, (i) if said surface includes a portion that contains at least 45 % of aluminum, said composition according to claim 10 additionally 25 comprises fluorine containing constituents in an amount so as to result in a value from about 400 to about 600 ppm of free fluoride as measured by means of a fluoride sensitive electrode; and (ii) if said surface includes a portion that contains at least 85 % 30 of zinc but does not include any portion that contains at least 45 % of aluminum, said

composition according to claim 10 additionally comprises a content of fluosilicate that is from about 1.10 to about 1.40 ppt, and said composition according to claim 10 has a free fluoride value that is not greater than about 20 ppm as measured by means of a fluoride sensitive electrode.

5 12. A process for forming a phosphate conversion coating on a surface selected from the group consisting of at least one of iron, steel, zinc-iron alloy, galvanized steel and other predominantly zinciferous surfaces, and aluminum and its alloys that contain at least 45 % by weight of aluminum, said process comprising contacting the surface with a composition according to claim 9 at a temperature from about 35 to about 70 °C for a time not greater than 100 seconds, said composition according to claim 9 having a Free Acid content from about 0.6 to about 1.5 points, and a Total Acid content from about 15 to about 40 points; wherein, (i) if said surface includes a portion that contains at least 45 % of aluminum, said composition according to claim 9 additionally comprises fluorine containing constituents in an amount so as to result in a value from about 250 to about 1200 ppm of free fluoride as measured by means of a fluoride sensitive electrode; and (ii) if said surface includes a portion that contains at least 85 % of zinc but does not include any portion that contains at least 45 % of aluminum, said composition according to claim 9 additionally comprises a total content of fluoborate, fluosilicate, fluotitanate, and fluozirconate that is from about 0.5 to about 2.5 ppt, and said composition according to claim 9 has a free fluoride value that is not greater than about 100 ppm as measured by means of a fluoride sensitive electrode.

10 13. A process for forming a phosphate conversion coating on a surface selected from the group consisting of at least one of iron, steel, zinc-iron alloy, galvanized steel and other predominantly zinciferous surfaces, and aluminum and its alloys that contain at least 45 % by weight of aluminum, said process comprising contacting the surface with a composition according to claim 8 at a temperature from about 35 to about 70 °C for a time not greater than 100 seconds, said composition according to claim 8 having a Free Acid content from about 0.6 to about 1.5 points, and a Total Acid content from about 15 to about 40 points; wherein, (i) if said surface includes a portion that contains at least 45 % of aluminum, said composition according to claim 8 additionally comprises fluorine containing constituents in an amount so as to result in a value from

about 250 to about 1200 ppm of free fluoride as measured by means of a fluoride sensitive electrode; and (ii) if said surface includes a portion that contains at least 85 % of zinc but does not include any portion that contains at least 45 % of aluminum, said composition according to claim 8 additionally comprises a total content of fluoborate, fluosilicate, fluotitanate, and fluozirconate that is from about 0.5 to about 2.5 ppt, and said composition according to claim 8 has a free fluoride value that is not greater than about 100 ppm as measured by means of a fluoride sensitive electrode.

14. A process for forming a phosphate conversion coating on a surface selected from the group consisting of at least one of iron, steel, zinc-iron alloy, galvanized steel and other predominantly zinciferous surfaces, and aluminum and its alloys that contain at least 45 % by weight of aluminum, said process comprising contacting the surface with a composition according to claim 7 at a temperature from about 35 to about 70 °C for a time not greater than 100 seconds, said composition according to claim 7 having a Free Acid content from about 0.2 to about 1.5 points, and a Total Acid content from about 15 to about 40 points; wherein, (i) if said surface includes a portion that contains at least 45 % of aluminum, said composition according to claim 7 additionally comprises fluorine containing constituents in an amount so as to result in a value from about 250 to about 1200 ppm of free fluoride as measured by means of a fluoride sensitive electrode; and (ii) if said surface includes a portion that contains at least 85 % of zinc but does not include any portion that contains at least 45 % of aluminum, said composition according to claim 7 additionally comprises a total content of fluoborate, fluosilicate, fluotitanate, and fluozirconate that is from about 0.5 to about 2.5 ppt, and said composition according to claim 7 has a free fluoride value that is not greater than about 100 ppm as measured by means of a fluoride sensitive electrode.

15. A process for forming a phosphate conversion coating on a surface selected from the group consisting of at least one of iron, steel, zinc-iron alloy, galvanized steel and other predominantly zinciferous surfaces, and aluminum and its alloys that contain at least 45 % by weight of aluminum, said process comprising contacting the surface with a composition according to claim 6 at a temperature from about 35 to about 70 °C for a time not greater than 100 seconds, said composition according to claim 6 having a Free Acid content from about 0.2 to about 1.5 points, and a Total Acid content from

about 15 to about 40 points; wherein, (i) if said surface includes a portion that contains at least 45 % of aluminum, said composition according to claim 6 additionally comprises fluorine containing constituents in an amount so as to result in a value from about 250 to about 1200 ppm of free fluoride as measured by means of a fluoride sensitive electrode; and (ii) if said surface includes a portion that contains at least 85 % of zinc but does not include any portion that contains at least 45 % of aluminum, said composition according to claim 6 additionally comprises a total content of fluoborate, fluosilicate, fluotitanate, and fluozirconate that is from about 0.5 to about 2.5 ppt, and said composition according to claim 6 has a free fluoride value that is not greater than about 100 ppm as measured by means of a fluoride sensitive electrode.

16. A process for forming a phosphate conversion coating on a surface selected from the group consisting of at least one of iron, steel, zinc-iron alloy, galvanized steel and other predominantly zinciferous surfaces, and aluminum and its alloys that contain at least 45 % by weight of aluminum, said process comprising contacting the surface with a composition according to claim 5 at a temperature from about 35 to about 70 °C for a time not greater than 100 seconds, said composition according to claim 5 having a Free Acid content from about 0.2 to about 1.5 points, and a Total Acid content from about 15 to about 40 points; wherein, (i) if said surface includes a portion that contains at least 45 % of aluminum, said composition according to claim 5 additionally comprises fluorine containing constituents in an amount so as to result in a value from about 250 to about 1200 ppm of free fluoride as measured by means of a fluoride sensitive electrode; and (ii) if said surface includes a portion that contains at least 85 % of zinc but does not include any portion that contains at least 45 % of aluminum, said composition according to claim 5 additionally comprises a total content of fluoborate, fluosilicate, fluotitanate, and fluozirconate that is from about 0.5 to about 2.5 ppt, and said composition according to claim 5 has a free fluoride value that is not greater than about 100 ppm as measured by means of a fluoride sensitive electrode.

17. A process for forming a phosphate conversion coating on a surface selected from the group consisting of at least one of iron, steel, zinc-iron alloy, galvanized steel and other predominantly zinciferous surfaces, and aluminum and its alloys that contain at least 45 % by weight of aluminum, said process comprising contacting the surface with

a composition according to claim 4 at a temperature from about 35 to about 70 °C for a time not greater than 100 seconds, said composition according to claim 4 having a Free Acid content from about 0.2 to about 1.5 points, and a Total Acid content from about 15 to about 40 points; wherein, (i) if said surface includes a portion that contains at least 45 % of aluminum, said composition according to claim 4 additionally comprises fluorine containing constituents in an amount so as to result in a value from about 250 to about 1200 ppm of free fluoride as measured by means of a fluoride sensitive electrode; and (ii) if said surface includes a portion that contains at least 85 % of zinc but does not include any portion that contains at least 45 % of aluminum, said composition according to claim 4 additionally comprises a total content of fluoborate, fluosilicate, fluotitanate, and fluozirconate that is from about 0.5 to about 2.5 ppt, and said composition according to claim 4 has a free fluoride value that is not greater than about 100 ppm as measured by means of a fluoride sensitive electrode.

18. A process for forming a phosphate conversion coating on a surface selected from the group consisting of at least one of iron, steel, zinc-iron alloy, galvanized steel and other predominantly zinciferous surfaces, and aluminum and its alloys that contain at least 45 % by weight of aluminum, said process comprising contacting the surface with a composition according to claim 3, wherein, in said composition according to claim 3: the concentration of component (A) is from about 0.40 to about 2.0 ppt; the concentration of component (C) is from about 0.2 to about 25 mM/kg; the concentration of component (D) is from about 5 to about 200 ppm; if said surface includes a portion that contains at least 45 % of aluminum, said composition additionally comprises fluorine containing constituents in an amount so as to result in a value from about 250 to about 1200 ppm of free fluoride as measured by means of a fluoride sensitive electrode; if said surface includes a portion that contains at least 85 % of zinc but does not include any portion that contains at least 45 % of aluminum, said composition additionally comprises a total content of fluoborate, fluosilicate, fluotitanate, and fluozirconate that is from about 0.5 to about 2.5 ppt, and said composition has a free fluoride value that is not greater than about 100 ppm as measured by means of a fluoride sensitive electrode; and said composition has a Free Acid content from about 0.2 to about 1.5 points and a Total Acid content from about 15 to about 40 points.

19. A process for forming a phosphate conversion coating on a surface selected from the group consisting of at least one of iron, steel, zinc-iron alloy, galvanized steel and other predominantly zinciferous surfaces, and aluminum and its alloys that contain at least 45 % by weight of aluminum, said process comprising contacting the surface with a composition according to claim 2, wherein, in said composition according to claim 2: the concentration of component (A) is from about 0.2 to about 2.0 ppt; the concentration of component (C) is from about 0.1 to about 50 mM/kg; the concentration of component (D) is at least about 5 ppm; if said surface includes a portion that contains at least 45 % of aluminum, said composition additionally comprises fluorine containing constituents in an amount so as to result in a value from about 250 to about 1200 ppm of free fluoride as measured by means of a fluoride sensitive electrode; if said surface includes a portion that contains at least 85 % of zinc but does not include any portion that contains at least 45 % of aluminum, said composition additionally comprises a total content of fluoborate, fluosilicate, fluotitanate, and fluozirconate that is from about 0.5 to about 2.5 ppt and said composition has a free fluoride value that is not greater than about 100 ppm as measured by means of a fluoride sensitive electrode; and said composition has a Free Acid content from about 0.2 to about 1.5 points and a Total Acid content from about 15 to about 40 points.

20. A process for forming a phosphate conversion coating on a metal surface, said process comprising contacting the surface with a composition according to claim 1, wherein, in said composition according to claim 1: the concentration of component (A) is from about 0.2 to about 2.0 ppt; the concentration of component (B) is from about 5 to about 100 ppt; the concentration of component (C) is from about 0.2 to about 25 mM/kg; the concentration of component (D) is from about 5 to about 200 ppm; and said composition has a Free Acid content from about 0.1 to about 3 points and a Total Acid content from about 15 to about 50 points.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/17086

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C23C 22/17

US CL : 148/251

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/251

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,659,395 (SUGMA ET AL) 21 April 1987	-
A	US, A, 4,882,216 (USHIO ET AL) 21 November 1989	
A	US, A, 3,837,928 (MORRISON) 24 September 1974	

Further documents are listed in the continuation of Box C.

See patent family annex.

•	Special categories of cited documents:	“T”	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
•“A”	document defining the general state of the art which is not considered to be of particular relevance		
•“E”	earlier document published on or after the international filing date	“X”	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
•“L”	document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	“Y”	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
•“O”	document referring to an oral disclosure, use, exhibition or other means	“Z”	document member of the same patent family
•“P”	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

04 JANUARY 1997

Date of mailing of the international search report

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